Uniform, High Aspect Ratio Fiber-like Micelles and Block Co-micelles with a Crystalline π-Conjugated Polythiophene Core by Self-Seeding

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Ⓢ Supporting Information

ABSTRACT: Monodisperse fiber-like micelles with a crystalline π-conjugated polythiophene core with lengths up to ca. 700 nm were successfully prepared from the diblock copolymer poly(3-hexylthiophene)-*block*-polystyrene using a one-dimensional self-seeding technique. Addition of a polythiophene block copolymer with a different corona-forming block to the resulting nanofibers led to the formation of segmented B-A-B triblock co-micelles by crystallization-driven seeded growth. The key to these advances appears to be the formation of a relatively defect-free crystalline micelle core under the self-seeding conditions.

π-Conjugated polymers such as poly(3-alkylthiophene)s (P3ATs) have been studied extensively due to their potential applications in optoelectronic devices[1] such as field-effect transistors[2] and solar cells.[3] Rod−coil block copolymers containing a polythiophene segment form highly ordered stacked structures in thin films[4] and provide an enhanced interfacial area for charge separation as well as an efficient pathway for charge transport.[5] Previous studies have shown that polythiophene block copolymers self-assemble in solution to form micelles with a variety of morphologies including fibers,[6] spheres,[7] vesicles,[8] helical structures,[9] ribbons,[10] and branched hierarchical structures.[6,11] Among these, fiber-like micelles containing a conductive core are of particular interest. For applications as conductive nanowires, uniform samples of easily processed nanofibers with controllable length and structure are highly desirable.[12] Significantly, fibers formed by block copolymers show significantly higher colloidal stability than homopolymer analogues, which facilitates the use of solution processing protocols. However, control over the length of P3AT block copolymer nanofibers is limited at present.

Systematic methods have recently been reported that allow structure control of fiber-like micelles formed by self-assembly of block copolymers containing a crystallizable core-forming block. For example, we have recently shown that a range of polyferrocenylsilane (PFS) block copolymers (PFS-*b*-PI, where PI = polyisoprene; PFS-*b*-PDMS, where PDMS = polydimethylsiloxane; etc.) form cylindrical micelles with a crystalline PFS core in solvents that are selective for the non-PFS block.[13] The most striking feature of these nanomaterials is that the ends of the crystalline PFS core remain active for further epitaxial crystallization upon the addition of further unimer (i.e.,

molecularly dissolved polymer).[14] By using monodisperse short micelles (referred to as "seeds"), this crystallization-driven self-assembly (CDSA) process has been used to obtain monodisperse cylinders with lengths controlled up to several micrometers by variation of the unimer-to-seed ratio.[15] This "living self-assembly" approach resembles a living covalent polymerization, and it is also possible to prepare complex micelle architectures with segmented coronas including "barcode" micelles,[16] multiblock micelles with different cores,[17] and non-centrosymmetric structures.[18,19] The CDSA process has been extended to the preparation of fiber-like micelles with other core-forming blocks,[19a,b] including polycaprolactone,[20] polyacrylonitrile,[21] polylactide,[22] and polyethylene.[23]

Extending these methods to semicrystalline, conjugated polymers would provide a facile route to monodisperse nanowires with attractive optoelectronic properties. Using a poly(3-hexylthiophene) diblock copolymer, P3HT-*b*-PDMS, we previously demonstrated that monodisperse fiber-like micelles could be obtained by CDSA from seed fragments generated by sonication of longer fibers. However, length control of the resulting micelles by seeded growth was limited to values of up to only ca. 250 nm.[24] Significantly, the inactivity of the core termini to further growth was attributed to the generation of defects due to the rapid crystallization of the P3HT block. Consistent with this explanation, our subsequent attempts to create longer fibers or block co-micelles from other P3HT block copolymers by CDSA was unsuccessful,[25] although for P3HT-*b*-P2VP (P2VP = poly(2-vinylpyridine)) slightly improved length control (up to ca. 300 nm) was achieved.[26] In this Communication we report on our preliminary results showing the controlled growth of monodisperse fibers of P3HT-*b*-PS (PS = polystyrene) of up to 700 nm in length by using an alternative, self-seeding method. The key to this advance is that the annealing inherent to this solution protocol allows the formation of a more defect-free crystalline core. Moreover, we show that the fibers accessible using this self-seeding approach allow for the first time the formation of block co-micelles with a P3HT core via CDSA involving the addition of unimers of a P3HT block copolymer with a different corona-forming block (Scheme 1).

In an attempt to improve the control resulting from CDSA with P3HT block copolymers, we explored the formation of fiber-like micelles using a 1D self-seeding approach. Self-seeding

Scheme 1. Illustration of the Experimental Design[a]
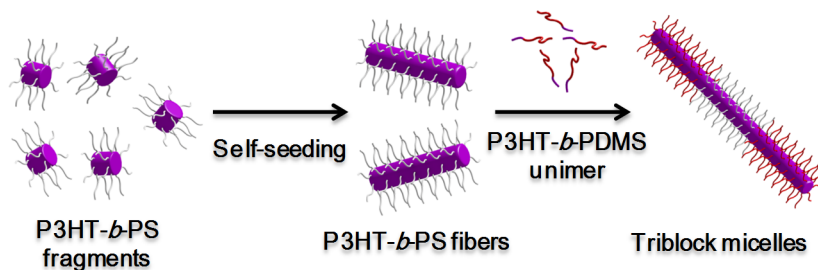
[a]Step 1: monodisperse fibers of P3HT-*b*-PS are prepared using a self-seeding approach. Step 2: triblock co-micelles with a P3HT core are obtained via living CDSA upon addition of P3HT-*b*-PDMS unimer.

is a process that can generate uniform polymer single crystals for both homopolymers[27] and diblock copolymers with a crystalline block.[28] Polymer crystals contain regions with different crystallinity and different melting points; when heated above their apparent melting or dissolution temperature, microscopic crystallites with high crystallinity survive. Upon cooling, these surviving nuclei can initiate crystal growth.[29] The size of polymer crystals in the bulk obtained after self-seeding depends only on the annealing temperature and not the length of time that the sample was annealed.[30] We recently reported the first example of 1D self-seeding of a PFS-*b*-PI diblock copolymer in the PI-selective solvent decane as a means of generating uniform samples of fiber-like micelles with lengths from 80 to 1700 nm.[31] Of key relevance to the present study is that we also showed that the self-seeding process helps to improve the crystallinity of the surviving PFS-*b*-PI seed micelles.[32] We also demonstrated that self-seeding of PFS-*b*-PI micelles can be achieved at room temperature by adding various amounts of a lower boiling point good solvent for both PFS and PI (e.g., THF) to the micelle solutions in decane, followed by slow evaporation.[32] These temperature- and solvent-induced 1D self-seeding techniques provide potentially important alternative methods with which to access uniform fiber-like micelles containing a relatively defect-free crystalline core. Recently, Reiter and co-workers showed the formation of crystalline nanofiber single crystals of P3HT homopolymer with controlled size over a very broad range via temperature-induced self-seeding.[33] These developments prompted us to explore the use of self-seeding methods to prepare uniform, colloidally stable high aspect ratio fiber-like P3HT block copolymer micelles.

We prepared regioregular P3HT$_{34}$-*b*-PS$_{175}$ (PS = polystyrene, M_n = 24 300 g/mol and M_w/M_n = 1.05) diblock copolymer via a Cu-catalyzed azide-alkyne cycloaddition reaction, using azide-terminated PS and alkyne end-functionalized P3HT homopolymers (see Supporting Information (SI) for further details).[34] Micelles of P3HT-*b*-PS were prepared by heating a mixture of this block copolymer (3 mg) and *n*-butyl acetate (BuAc, 10 mL) to 100 °C for 2 h, followed by slow cooling to 23 °C (ca. 1.5 °C/min). This process generated fiber-like micelles with lengths on the order of several micrometers (see TEM image in Figure 1A). However, these fiber-like micelles formed aggregates on the carbon film of the copper grid during solvent evaporation. This made it difficult to visualize individual micelles.[35] To solve this problem, samples were drop-cast as 1:1 mixtures of ca. 50 μL of sample solution with 1 mg/mL solution (ca. 50 μL) of PS$_{875}$ homopolymer (see SI for further information) in BuAc. We expected the PS homopolymer to function as a dispersion matrix for the P3HT-*b*-PS micelles during solvent evaporation. A
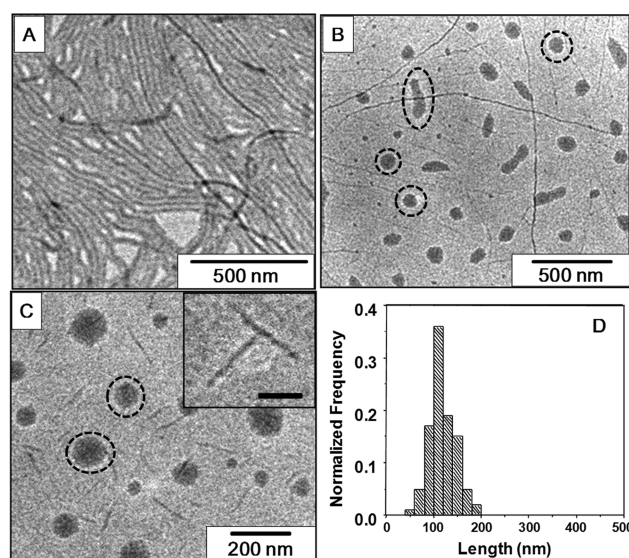

Figure 1. (A,B) Fiber-like micelles formed by the self-assembly of P3HT-*b*-PS in BuAc (c = 0.3 mg/mL): (A) aggregates of fibers and (B) fibers dispersed by PS$_{875}$ homopolymer. (C) P3HT-*b*-PS micelle fragments dispersed by PS. Inset shows two magnified micelle fragments; scale bar is 100 nm. The dark regions in (B,C) marked by dashed lines are aggregates of PS. (D) Contour length distribution of the micelle fragments in (C), L_n = 118 nm, L_w = 124 nm, L_w/L_n = 1.05, σ/L_n = 0.220.

representative TEM image of the P3HT-*b*-PS micelles with PS homopolymer is shown in Figure 1B. This illustrated that the approach was successful, as long, well-separated P3HT-*b*-PS micelles were observed. The representative dark regions marked by dashed lines in Figure 1B arise from the aggregation of the PS homopolymer.

To prepare small micelle fragments to function as precursors for the self-seeding experiments, the BuAc solution of P3HT-*b*-PS micelles was subjected to ultrasonication (160 W) in a water bath at 23 °C for two 15 min intervals. In Figure 1C, we show a representative TEM image of the micelle fragments dispersed with PS homopolymer on a carbon film. From the histogram of their length distribution (Figure 1D), we calculated the number- and weight-average lengths (L_n and L_w) and the standard deviation (σ) of the length distribution. These fragments in solution were stable, and their lengths and length distribution remained unchanged over a period of 6 months.

To carry out temperature-induced self-seeding experiments, we annealed aliquots (ca. 300 μL) of the solution of the P3HT-*b*-PS micelle fragments in an oil bath at different temperatures for 30 min, then quenched each solution into another oil bath at 35
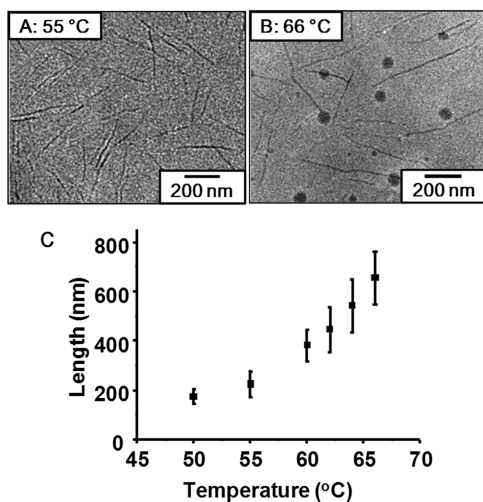
Figure 2. (A,B) TEM images of the P3HT-*b*-PS micelles dispersed by PS obtained by annealing the micelle fragments in BuAc at (A) 55 and (B) 66 °C for 30 min, followed by annealing at 35 °C for 24 h and cooling to 23 °C. (C) Number-average micelle length L_n vs annealing temperature. Error bars are the standard deviations σ for the length distribution.

°C and allowed the solution to age at 35 °C for 24 h. Each sample was then allowed to age at 23 °C for 24 h before TEM analysis. The purpose of allowing the sample to age at 35 °C was to prevent self-nucleation at 23 °C. Annealing the fragment solution at 35 °C for 24 h caused no change in the micelle fragments (see Table S1). As shown in the TEM images in Figure 2A,B for samples annealed at 55 and 66 °C, we obtained longer micelles with narrow length distribution (see Figure S7). The length information of all samples is summarized in Figure 2C, which shows the average contour length vs annealing temperature. These data illustrate that the length of the micelles increases with the annealing temperature, giving fibers up to values of ca. 700 nm with a narrow length distribution ($L_w/L_n < 1.05$). When the annealing temperature was too high (70 °C), we obtained micelles with non-uniform lengths, including micelles longer than 1 μm and micelles as short as 200 nm, as shown in the TEM image in Figure S8. Based on the initial length of the micelle fragments and the final length of micelles after the self-seeding, we could calculate the fraction of surviving fragments at each annealing temperature (see SI for discussion). From Figure S9, we can observe that, in the range of 50−66 °C, the fraction of surviving seeds decreased exponentially with increasing temperature. This is key characteristic of the self-seeding process.[30] We also performed experiments to examine the effect of annealing time on the micelle length. These indicated that increasing the annealing time had no significant effect on micelle length (Figure S10 and Table S2), as expected for a thermodynamically controlled process.[28] We also examined one of the micelle samples obtained by annealing the micelle fragments at 66 °C by laser confocal fluorescence microscopy. The resulting images of the micelles in BuAc are presented in Figure S11, where rod-like objects dispersed in solution can be observed.

We then examined the electronic and photoluminescence (PL) properties of P3HT-*b*-PS unimers dissolved in THF, the initially formed P3HT-*b*-PS micelles in BuAc, as well as the P3HT-*b*-PS micelles formed after the self-seeding process in BuAc (annealing temperature = 60 °C). The UV/vis spectra in Figure S12A revealed that the P3HT-*b*-PS unimers in THF showed an absorption at 440 nm. The two P3HT-*b*-PS fiber-like

micelle solutions showed a red-shifted absorption at 472 nm, characteristic of a more planar and highly conjugated main-chain conformation than in solution.[36] Moreover, the appearance of a shoulder at 600 nm indicated the crystalline ordering of the P3HT core, which results from the strong intermolecular interactions among regioregular P3HT chains.[37] Significantly, the peak at 600 nm for the micelles obtained after the self-seeding process appears to be more intense than that of the initial formed micelles, indicating that the annealing process improved the packing of the crystalline core.[32] The PL spectra of the three samples are presented in Figure S12B, where it is clear that the emission intensity of the micelles in BuAc was much lower than that of the unimers in THF at the same concentration, indicative of fluorescence quenching due to the aggregation of P3HT chains.[38] However, it is noteworthy that both of the P3HT-*b*-PS micelle solutions retained significant emission intensity.

We also found that solvent-induced self-seeding of P3HT-*b*-PS fibers could be achieved. Thus, micelle fragments of lower crystallinity could be selectively dissolved by adding various amounts of THF, a good solvent for both P3HT and PS. After the slow evaporation of THF at 23 °C, we obtained longer micelles with a narrow length distribution. The longest fibers we obtained in this way possessed $L_n = 687$ nm and $L_w/L_n = 1.04$, at initial THF volume fraction of ca. 54% (see Figure S13-15 and Table S3).

The uniform P3HT-*b*-PS fiber-like micelles that are obtained by the self-seeding protocols should, in principle, remain active for further growth, even when another P3HT block copolymer with a different corona block is added. On addition of a THF solution of P3HT$_{34}$-*b*-PDMS$_{236}$ (0.25 mL, 0.8 mg/mL) into a BuAc solution of P3HT-*b*-PS nanofibers with $L_n \approx 380$ nm (0.50 mL, 0.05 mg/mL) generated by self-seeding, B-A-B triblock co-micelles could be obtained. Prior to TEM analysis, the sample was treated with RuO$_4$, which selectively stains the P3HT core and PS corona. These structures are shown in Figure 3, in which
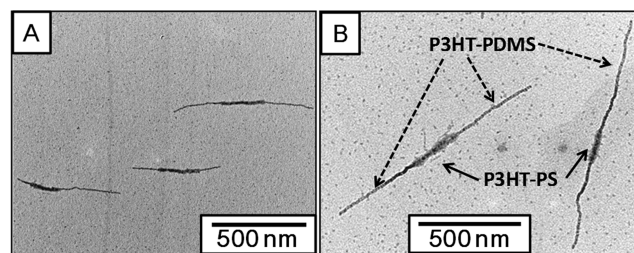

Figure 3. (A,B) TEM images of triblock co-micelles formed by adding unimer of P3HT-*b*-PDMS in THF into a BuAc solution of P3HT-*b*-PS, followed by evaporation of THF in air for 24 h. No PS homopolymer was added. The sample was stained by RuO$_4$. The blurry regions of the micelles are due to the staining of PS corona.

two thinner blocks of P3HT-*b*-PDMS grown from a wider central P3HT-*b*-PS block are evident. Additional, representative TEM images are shown in Figure S16A,B. However, we also noted some defects in the samples such as the formation of P3HT-*b*-PDMS homo-micelles, which are shown in Figure S16C−F.

In summary, we have demonstrated the successful extension of one-dimensional self-seeding to the preparation of uniform fiber-like micelles from a P3HT-*b*-PS diblock copolymer up to ca. 700 nm. This represents a significant advance over previous methods and we attribute this to the formation of more defect-free crystalline cores under the self-seeding conditions, an assertion

supported by the UV/vis data. We have also demonstrated the formation of the first block co-micelles containing a P3HT core by the seeded growth of P3HT-*b*-PDMS unimers from the termini of the P3HT-*b*-PS fiber-like micelles generated by self-seeding. These developments represent a substantial further step toward fine control of the structure of P3HT nanofibers, and work aimed at the formation of more complex multiblock structures and an exploration of their properties and applications is underway.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details; supporting figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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